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## Nucleation and growth of sodium colloids in NaCl under irradiation: theory and experiment

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A mechanism of radiation-induced emission of Schottky defects from extended defects proposed originally for metals has recently been applied to ionic crystals, where it is based on interactions of excitons with extended defects such as dislocations and colloids. Exciton trapping and decay at colloids may result in the emission of  $F$  centers and consequent shrinkage of the colloid. In the present paper, the radiation-induced emission of  $F$  centers is taken into account in the modeling of nucleation and growth of *sodium colloids* and *chlorine bubbles* in *NaCl* exposed to electron or gamma irradiation. The evolution of colloid and bubble number densities and volume fractions with increasing irradiation dose is modeled in the framework of a *modified rate theory* and compared with experimental data. Experimental values of the colloid volume fractions and number densities have been estimated on the basis of latent heat of melting of metallic Na obtained with combined differential scanning calorimetry experiments and atomic force microscopy investigations of metallic clusters.

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### 1 Introduction

Exposure of alkali halides to ionizing radiation results in the formation of nano-sized halogen “bubbles” by agglomeration of  $H$  centers and of complementary inclusions of metallic “*colloids*” formed by agglomeration of  $F$  centers.  $H$  and  $F$  centers are the primary radiation-induced Frenkel pairs in the halide sub-lattice created in the crystal bulk due to decay of self-trapped excitons [1]. The  $H$  center is a hole trapped at an interstitial halide ion, and an  $F$  center is a vacancy in the halide sub-lattice with a trapped electron. The cation sub-lattice is not damaged during primary displacement processes in the crystal bulk [1]. However, early experimental results on electron irradiated alkali halides such as *KCl* and *NaCl* [2] provided evidence for the formation of perfect dislocation loops, which require agglomeration of interstitial ions in both anion and cation sub-lattices. The first explanation for this phenomenon was given by Hobbs et al. [2], and it was based on the production of a molecular center (a halogen molecule occupying a stoichiometric divacancy) due to interaction between dislocations and two  $H$  centers. In 1977, Jain and Lidiard [3] have formulated a model, according to which, the *dislocation bias* for  $H$  centers was the driving force for the colloid growth in alkali halides in the same way as it is for *void growth in metals* under irradiation. The mechanism of dislocation climb [2] used in the Jain and Lidiard model, requires two  $H$  centers meeting each other at the dislocation core, and subsequently, the model was modified by Dubinko et al. [4], who suggested that a dislocation can climb due to the production of a  $V_F$  center (self-

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trapped hole neighboring a cation vacancy) induced by interactions between a dislocation and only one  $H$  center. Subsequent diffusion of  $V_F$  centers away from dislocations and recombination with  $F$  centers results in the formation of stoichiometric divacancies thus providing a driving force for the formation and growth of vacancy voids observed experimentally.

In this model, the void growth rate is determined by the flux of  $V_F$  centers and by the net flux of  $F$  centers (i.e. the difference between  $F$  and  $H$  center fluxes), which depends on the difference between the void bias and the mean bias of the system for the absorption of  $F$  centers. This difference is positive for void radii larger than a critical radius,  $R_V^{crit}$ , which is determined by the ratio of material constants related to the void and dislocation biases [4]:

$$R_V^{crit} = \frac{\alpha^{im} b}{\delta_d} \approx (1 \div 2) b \quad (1)$$

where  $b$  is the atomic spacing and  $\alpha^{im}$  is the constant associated with image interaction:

$$\alpha^{im} = (\alpha_H^{im} - \alpha_F^{im}), \quad \alpha_{F,H}^{im} = \left[ \frac{\mu(1+\nu)^2 \Omega_{F,H}^2}{36 \cdot k_B T (1-\nu) b^3} \right]^{1/3}, \quad (2)$$

$\delta_d$  is the dislocation bias for the absorption of  $H$  centers, which is determined by the ratio of the relaxation volumes associated with  $H$  and  $F$  centers,  $\Omega_H / |\Omega_F|$ :

$$\delta_d = \ln \left( \frac{\Omega_H}{|\Omega_F|} \right) / \ln \left( \frac{2}{L_H k_H} \right), \quad L_H = \frac{\mu b (1+\nu)}{3\pi k T (1-\nu)} \Omega_H \quad (3)$$

where  $\nu$  is the Poisson ratio,  $\mu$  is the shear modulus of the host matrix,  $k_H$  is the square root of the total sink strength for  $H$  centers,  $kT$  has its usual meaning.

The critical void radius  $R_V^{crit}$  is given by the same equation (1) as the critical colloid radius, and it is smaller than the radius of void nuclei produced by bubble-colloid collisions [4, 5]. Accordingly, one would expect all void nuclei to grow to visible sizes. The number density of the void nuclei,  $N_V^0$ , can be estimated as the product of the bubble number density,  $N_B \approx 10^{18} \div 10^{19} \text{ cm}^{-3}$  and the colloid volume fraction,  $V_C \approx 10^{-2} \div 10^{-1}$ :  $N_V^0 \approx N_B \times V_C \approx 10^{16} \div 10^{17} \text{ cm}^{-3}$ . However, the observed void number densities are about  $10^{13} \div 10^{14} \text{ cm}^{-3}$ , which means that only a very small part of void nuclei survive and grow to visible sizes. The physical reason for this low “survival” rate remained unaccounted in the previous model.

In a recent paper [6], an alternative mechanism of void and dislocation loop growth in alkali halides was considered, which was based on production of divacancies (Schottky defects) by interactions between dislocations and excitons, as was first suggested by Seitz in 1954 [7]. Voids can also emit divacancies due to the interaction with excitons, and so the balance between absorption and emission of divacancies determines the void evolution in this model, which has been shown to be in good agreement with experimental observations.

In the present paper, the exciton-induced emission of F-centers from colloids is taken into account in the calculation of colloid nucleation and growth rates in the framework of the modified rate theory [8]. The driving force of colloid growth is the large bias of halogen bubbles for absorption of  $H$  centers rather than the dislocation bias employed in the previous models [3, 4]. Thus, radiolysis (separation of chlorine and sodium into bubbles and colloids) and the development of stoichiometric defects (voids and dislocations) occur simultaneously but relatively independently. The only important “bridge” between these subsystems is bubble nucleation, which starts from recombination of  $H$  centers and divacancies since the homogeneous nucleation rate due to recombination of  $H$  centers is negligible.

## 2 Excitonic production of Frenkel and Schottky defects

According to Seitz [7], an exciton may cause movement of nearby dislocation jogs, resulting in the creation of equal numbers of anion and cation vacancies - Schottky defects (SD). Owing to the heat generated locally during exciton annihilation, the jog can be displaced while a divacancy arises in the lattice. In a previous paper [8], we have incorporated the excitonic production mechanism of both Frenkel and Schottky defects in rate theory and evaluated so called *local equilibrium concentrations* of SD,  $C_{sS}^{eq}$ , (almost) spherical (colloids and voids), cylindrical (dislocations) and planar (grain boundaries) sinks, where subscript “s” designates the type of SD ( $s=v$  for divacancies,  $s=F$  for  $F$  centers) and “S” is the type of the sink ( $S=V$  for voids,  $S=F$  for colloids,  $S=B$  for bubbles and  $S=D$  for dislocations).

In absence of the radiation field, one has  $C_{sS}^{eq} = C_{sS}^{th}$ , which can be obtained from thermodynamics. Under irradiation,  $C_{sS}^{eq}$  is generally given by the sum of  $C_{sS}^{th}$  and  $C_{sS}^{irr}$ , which is due to the radiation-induced emission of SD's. Here,  $C_{sS}^{irr}$  has a purely kinetic origin and can be expressed via the *radiation-induced local emission rate* of SD,  $K_{sS}^{irr}$  [8]:

$$K_{vD}^{irr} = \frac{K_{FP}^0}{P_{FP}} \frac{Z_{ex}^D l_{ex}^2}{2\pi r_D b}, \quad Z_{ex}^D = \frac{2\pi}{\ln(\pi/k_D r_D)}, \quad C_{vD}^{irr} = K_{vD}^{irr} \times \frac{b^2}{D_v} \quad (4)$$

$$K_{vV}^{irr} = \frac{K_{FP}^0}{P_{FP}} \frac{l_{ex}^2}{b R_V}, \quad C_{vV}^{irr} = K_{vV}^{irr} \times \frac{b^2}{D_v} \quad (5)$$

where  $l_{ex}$  is the mean free diffusion path of the exciton i.e. the average displacement of the exciton before it decays,  $P_{FP}$  is the probability of the formation of a Frenkel pair (FP) in the anion sub-lattice due to exciton decay in the bulk,  $K_{FP}^0$  is the FP production rate in the bulk crystal,  $Z_{ex}^D$  and  $r_D$  are the dislocation capture efficiency and capture radius for excitons and  $D_v$  is the divacancy diffusion coefficient.

The difference between the mean divacancy concentration,  $\bar{C}_v$ , and the local equilibrium concentrations at voids is the driving force for the void growth (or shrinkage), and its rate is given by [6]

$$\frac{dR_v}{dt} = \frac{D_v}{R_v} (\bar{C}_v - C_{vV}^{eq}) \quad (6)$$

The colloid growth rate is determined by the difference between the bias-induced absorption [4] and the exciton-induced emission [8] of  $F$  centers:

$$\frac{dR_C}{dt} = \frac{1}{R_C} (Z_F^C(R_C) D_F \bar{C}_F - Z_H^C(R_C) D_H \bar{C}_H - Z_F^C(R_C) D_F C_{FC}^{eq}) \quad (7)$$

where  $\bar{C}_F, \bar{C}_H$  are the mean concentrations of  $F$  and  $H$  centers, respectively, which are determined by the usual rate equations, and  $Z_{F,H}^C(R_C)$  are the colloid capture efficiencies for  $F$  and  $H$  centers [4]:

$$Z_{F,H}^C(R_C) = 1 + \frac{\alpha_{F,H}^{im} \cdot b}{R_C} \quad (8)$$

Bubble growth is due to the difference between the bias-induced absorption of  $H$  centers, since the emission of  $H$  centers requires higher energies than for  $F$  centers and therefore it has not been taken

into account in the present model. Accordingly, we find the following expression for the bubble growth rate

$$\frac{dR_B}{dt} = \frac{1}{R_B} (Z_H^B(R_B) D_H \bar{C}_H - Z_F^B(R_B) D_F \bar{C}_F) \quad (9)$$

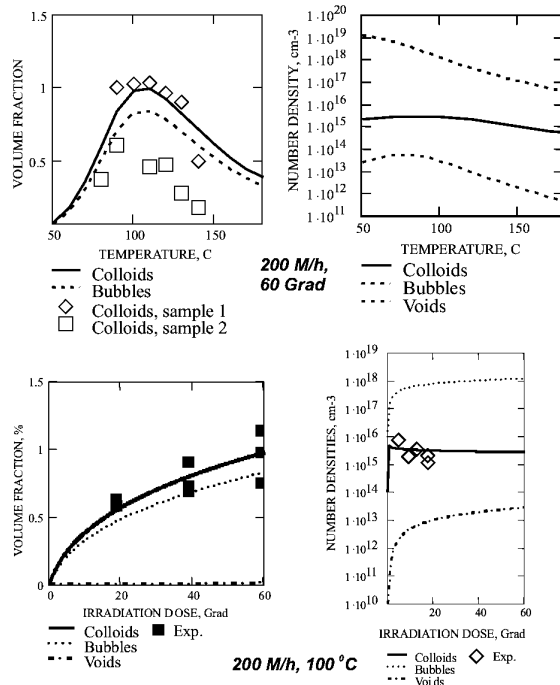
$$Z_{F,H}^B(R_B) = 1 + \frac{(\alpha_{F,H}^{im} - \alpha_{F,H}^d) b}{R_B} + \frac{\alpha_{F,H}^\mu b^2}{R_B^2} \quad (10)$$

where  $\alpha_{F,H}^d$  and  $\alpha_{F,H}^\mu$  are the constants associated with the stress-induced diffusion anisotropy and the modulus interaction, respectively [4].

The bubble growth rate increases with decreasing bubble radius, and so they can grow from molecular centers formed by recombination of  $H$  centers and divacancies. On the other hand, the growth rates of colloids and voids decrease with decreasing size and they are negative below some critical radius, which determines the rate of their nucleation. The critical colloid radius is small (see eq. (1)), and so they can nucleate homogeneously at a rather high rate [9]. At the same time, the critical void radius is comparatively large [6]

$$R_V^{crit} = \frac{2\pi r_D}{Z_{ex}^D} \approx (3 \div 4) b \quad (11)$$

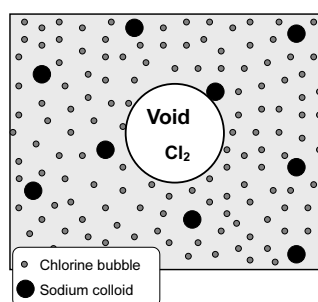
and so they can be formed only from sub-critical void nuclei produced as a result explosive recombination of colloids and bubbles [6]. The present model provides a possibility to evaluate nucleation and the growth rate of colloids, bubbles and voids in the framework of rate theory [8]. The results of the model calculations are shown in Fig. 1 together with experimental data available up to date.



**Fig. 1** Temperature dependence of the volume fraction and the number density of extended defects in NaCl electron irradiated up to different dose levels at a dose rate of 200 Mrad/hour.

### 3 Conclusion

According to the present model, chlorine bubbles are the most finely dispersed ED in the system (the inter-bubble spacing is typically a few nm) implying that they start to collide with growing voids first, filling them with chlorine gas (fig. 2) The chlorine molecules in the “bubbles” are in a solid or liquid state due to a super high pressure (in the GPa range), but after collision with a void it is in the vapor state. Chlorine accumulation in voids provides a very important possibility for explosive back reactions with metallic sodium when growing voids start hitting colloids, which results in void-crack production and ultimately in explosive fracture of the material [5].



**Fig. 2** Illustration of the distribution of chlorine bubbles, sodium colloids and voids in irradiated NaCl crystals. The bubble size is ~1-2 nm; the colloid size ~ inter-bubble spacing ~5-10 nm; the void size is about inter-colloid spacing ~20-30 nm, when collisions with colloids start.

From a more general perspective, the mechanisms of void and dislocation loop growth and colloid shrinkage in alkali halides considered above are characteristic manifestations of radiation-induced emission of Schottky defects, which may be responsible for a number of various radiation effects such as the void dissolution and swelling saturation in irradiated metals [10], irradiation creep [11] and possibly the void ordering [12].

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